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CHAPTER VIII

See also: Nickel(II) fluoride, synthesis 47A
Cobalt(III) flouride, synthesis 47B

51. ANHYDROUS IRON(III) CHLORIDE

(Ferric Chloride)

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

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The most convenient laboratory method for the preparation of iron(III) chloride involves the direct combustion of metallic iron in dry chlorine.[1] The directions given here are suitable for preparing this material in 100-g. quantities or, by simple modification of the apparatus, in larger amounts.

Iron(III) chloride has been employed as a catalyst in such reactions as the Friedel-Crafts synthesis,[2] the preparation of alkyl chlorides from olefins (other than ethylene), and the hydrogenation[3] and chlorination of aromatic compounds.[4]

Procedure A (Small Quantities)

The apparatus depicted in Fig. 40 is made of 28-mm. pyrex tubing and consists of a reaction chamber *D* and three collection chambers *E*, *F*, and *G*, each 25 cm. in length joined by 5-cm. constricted segments that should not be less than 10 mm. in diameter. Just before the reaction is carried out the tube is flamed, while a current of dry air is passed through it, to remove all moisture.

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Thirty-five and one-half grams of pure iron wire (No. 36)* is dried at 110°, cooled in a desiccator and then placed in the reaction chamber *D*. Chlorine gas is passed through the sulfuric acid wash bottle *A* and through a drying tube *C* containing phosphorus(V) oxide. Between these two vessels, the train is provided with a side tube *B* dipping into sulfuric acid to act as a safety outlet for the chlorine in event the combustion tube becomes clogged. From *C* the chlorine is passed through the combustion tube and thence through a container of calcium chloride *H* to prevent the entrance of moisture. The unreacted chlorine passes through a trap *I* and is absorbed by sodium hydroxide in *J*.

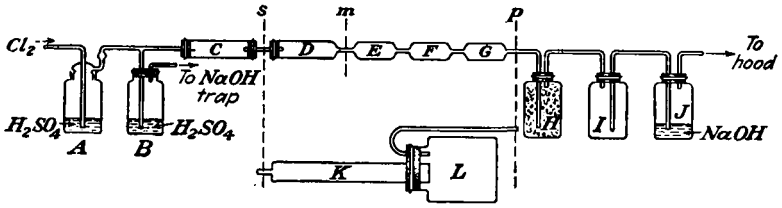

FIG. 40. Apparatus for preparation of anhydrous iron(III) chloride.

After the air has been displaced with chlorine, the segment *D* containing the iron wire is heated gently. The reaction takes place readily and iron(III) chloride soon begins to fill the reaction chamber. After the reaction has ceased, the product is sublimed by careful heating in an atmosphere of chlorine from the reaction chamber into the two succeeding segments *E* and *F*. Care is taken that none of the constricted portions become clogged. The flow of chlorine is stopped and the tube sealed off at the point *m*. The opposite end of the tube at *p* is now attached to the vacuum line through a sodium hydroxide trap and the excess of chlorine is removed. The tube is then sealed at *p*. The anhydrous chloride is then distributed by sublimation into the tubes as desired. If it is desired to collect the total yield in one compartment, the end segments may be

* Finer wire should not be used, as the reaction is apt to become too vigorous.

heated in an electric tube furnace and each one may be sealed off after it has been emptied.

The yield is nearly quantitative. Since it is difficult to sublime the last bit of iron(III) chloride completely from the reaction chamber, there is usually about a 3 per cent loss at this point. The material is not absolutely pure, as it contains small amounts of iron(II) chloride, but is suitable for most work. An absolutely pure product may be obtained by repeated sublimation in an atmosphere of chlorine.

Procedure B (Larger Quantities)

That portion of the apparatus from *s* to *p* is replaced by a pyrex combustion tube *K* connected through a rubber stopper to a wide-mouthed bottle *L* (which, after removal from the apparatus, can be closed with a ground-glass stopper). This bottle should be thoroughly dried in an oven at 125° before the synthesis is carried out. The reaction tube *K* is flamed while dry air is passed through it. For 70 g. of iron wire, a 1-l. bottle should be used. Number 36 iron wire is employed, as before. The iron(III) chloride, as it is formed, is sublimed into the bottle.

The excess chlorine is conducted to trap *H* through a tube that should be at least 1 cm. in diameter. When the reaction is complete, the bottle *L* is disconnected from the apparatus and immediately stoppered.

Properties

Anhydrous iron(III) chloride forms crystals that are dark green in reflected light and purple-red in transmitted light. The compound melts at 306° and can be volatilized at a slightly lower temperature. Vapor density measurements show that iron(III) chloride is dimeric at 440°, but monomeric above 750°. Measurements at these higher temperatures are complicated by the fact that appreciable dissociation into iron(II) chloride and chlorine also takes place. On exposure to air the anhydrous salt is readily transformed to the yellow-brown 6-hydrate. Accordingly,

if it is necessary to transfer the anhydrous material from one vessel to another, the operation should be carried out in a "dry box," or according to the procedure described by Bergstrom.[1]

Anhydrous iron(III) chloride is soluble in many solvents, especially those which can coordinate with it, such as the alcohols, ethers, ketones, pyridine, benzonitrile, phosphorus(III) bromide, sulfur dioxide, and sulfuryl chloride.

References

1. BERGSTROM: *J. Am. Chem. Soc.*, **46**, 1547 (1924).
2. GALLAY and WHITBY: *Can. J. Research*, **2**, 31 (1930).
3. KLING and FLORENTIN: *Compt. rend.*, **184**, 822 (1927).
4. MASON, SMALE, THOMPSON, and WHEELER: *J. Chem. Soc.*, **1931**, 3150.

52. HEXAMMINENICKEL(II) BROMIDE AND HEXAMMINENICKEL(II) IODIDE

$$[Ni(OH)_2]_4 \cdot H_2O + 8HX \rightarrow 4NiX_2 + 9H_2O$$
$$NiX_2 + 6NH_3 \rightarrow [Ni(NH_3)_6]X_2$$

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The hexammines of the bromide and iodide of nickel(II) provide a convenient means of introducing nickel(II) ion into liquid ammonia solutions under anhydrous conditions.[1,2] Although the literature includes numerous references to the preparation of these compounds from the corresponding anhydrous salts or their hydrates,[2–4] details of procedure have not been specified. The simple procedure outlined below provides these salts in high yield and high purity.

Procedure

Twenty grams of reagent-grade hydrated nickel(II) hydroxide,‡ $[Ni(OH)_2]_4 \cdot H_2O$, is dissolved in 55 ml. of warm

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‡ If the solid hydroxide is not available, it may be prepared conveniently by precipitation from a solution of a nickel(II) salt such as the sulfate by addition of sodium hydroxide, followed by thorough washing.